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RESEARCH

Kinetics study of platinum and base metals precipitation in gas–liquid chloride system

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Abstract The use of dissolved sulphur from gaseous phase was tested for its ability to precipitate platinum ions in chloride system with alterations in the parameters such as metal ion concentration, hydrochloric acid concentration, pressure and temperature. The precipitation process was analysed on the basis of mass transfer coefficient, diffusivity models and also by absorption kinetic models. The maximum physical and reactive absorption capacity for sulphur dioxide was found to be 0.015 and 0.018 mol/L, respectively, at 298.15 K and 1.125 bars in a short contact time of 10 min. Based on the sulphur dioxide solubility data in gas–liquid system for both physical and reactive absorption conditions, the introduction of sulphur atoms in the chloride system was achieved. The mass transfer coefficients obtained for all metal ions were in the range 0.10–0.26 min^{-1}, while the diffusivity of SO_2 at different temperatures and pressures was found to be in the range $(2.36–3.43) \times 10^{-9}$ and $(1.36–2.22) \times 10^{-9}$ m^2s^{-1}, respectively. Thermodynamic parameters such as the changes in Gibbs free energy, enthalpy and entropy were also evaluated. The results indicated that the precipitation of platinum and base metals in gas–liquid (G–L) chloride system was an endothermic process.

Keywords Diffusivity · Mass transfer coefficient · Platinum · Precipitation · Sulphur dioxide

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Introduction

Global concerns about the impact of toxic gases and effluents on the environment have led to the platinum industry leaders to adopt new strategies of recycling or capturing mine waste. Carbon dioxide (CO_2), for example, from coal-fired power stations and the environment is currently being captured and stored in coal seams underground [1, 2]. Hesselmann and Hough have reported the development of the technology of converting toxic oxides of nitrogen (NO_x) from well-designed boiler burners using ammonia-based reagent and hydrocarbon into a flue gas containing NO_x and some O_2 [3]. They found that at elevated temperatures the hydrocarbon auto ignites, forming plasma, and creating radicals. These radicals catalysed the NO_x reduction reactions—autocatalysis—and the resulting flue gas was found to contain very low NO_x and small level of ammonia slip. Other researchers have also reported on the concept of capturing SO_2 from fluidized-bed reactors during coal gasification using dolomite [4]. However, there is scanty literature on the application of acidic chloride solutions as a means of capturing SO_2 from flue gases and the same time precipitate the precious metals as sulphides. It is established that dissolved sulphur reacts readily with base and precious metal ions to form metal sulphides [5–7]. In industrial sedimentation processes, reduction of metal ions such as sulphides is accomplished by contacting metal-rich solutions with commercial H_2S or SO_2 gases. To utilize commercial SO_2 gases or other sulphur-bearing gases for recovering metals from solution, it is necessary to put in place effective mechanisms for capturing and solubilizing gases.

The conventional separation and purification of platinum group metals (PGMs) in industry combines liquid–liquid precipitation in alkaline media, distillation (boiling

off volatile metals) and ion exchange in resin columns. Distillation is an energy-intensive process and ion exchange process requires huge operational costs due to imported resins. Resins are not only expensive but also toxic. The concept of selective gas–liquid precipitation of PGMs using waste sulphide gases from the smelter is more attractive.

In this study, the concept of capturing SO_2 from industrial flue gases by means of acidic chloride solutions has been assessed in a continuous process. The main postulate is that dissolved sulphides can serve as precipitants for platinum ions in chloride system. The effects of different parameters such as initial metal ion concentration, hydrochloric acid concentration, pressure and temperature have been investigated. The absorption rates and thermodynamic parameters were deduced from the absorption measurements.

Theory of absorption kinetics

The absorption kinetic studies in G–L process were conducted to establish the parameters which affect metal (Fe, Co and Cr) precipitation in G–L chloride systems. The study was predominantly concerned with the precipitation rates of Pt as this was the main target metal in the mixed chloride systems. Furthermore, the mass transfer coefficients (K_L), diffusivities (D_L), absorption rates (N), activation energy (E_a) and the thermodynamic properties (ΔH, ΔG and ΔS) associated with platinum were quantified.

In G–L process using the continuous stirred tank reactor (CSTR), chloride solutions of Pt and base metals are used to absorb SO_2 to form solid products (precipitates). There are several reactions and physical steps which may affect the rate of SO_2 absorption within acidic chloride solutions. These include [8, 9]:

(a) The diffusion of SO_2 through the gas film near the gas–liquid interface.
(b) The dissolution of SO_2 in liquid phase (gas–liquid equilibrium):

$$SO_{2(g)} \leftrightarrows SO_{2(aq)} \quad (1)$$

(c) The first dissociation of $SO_{2(aq)}$:

$$SO_{2(aq)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)} \quad (2)$$

$$H_2SO_{3(aq)} \leftrightarrows H^+_{(aq)} + HSO^-_{3(aq)} \quad (3)$$

(d) The second dissociation of SO_2:

$$HSO^-_{3(aq)} \leftrightarrows H^+_{(aq)} + [SO_3]^{2-}_{(aq)} \quad (4)$$

$$SO_{2(g)} + 2[OH]^-_{(aq)} \leftrightarrows [SO_3]^{2-}_{(aq)} + H_2O_{(aq)} \quad K = 1.74 \text{ x } 10^{-2} \quad (5)$$

$$SO_{2(g)} + [SO_3]^{2-}_{(aq)} + H_2O_{(aq)} \leftrightarrows 2[HSO_3]^-_{(aq)} \quad K = 9.10 \text{ x } 10^{-10} \quad (6)$$

$$[HSO_3]^-_{(aq)} + [OH]^-_{(aq)} \leftrightarrows [SO_3]^{2-}_{(aq)} + H_2O_{(aq)} \quad K = 6.24 \text{ x } 10^{-8} \quad (7)$$

where K is the equilibrium constant. The equilibrium constant is important because it gives where the equilibrium lies. The larger the equilibrium constant, the further the equilibrium lies towards the products. Therefore, on the basis of reactions (5) and (7), $[SO_3]^{2-}$ ions are the main product when SO_2 reacts with water $[OH]^-$ molecules in a few stages. This suggests that at equilibrium, most of the chemical species present ($[SO_3]^{2-}$) are products. From this view, it is possible to correlate the absorption rate (**N**) of SO_2 with SO_3^{2-} in the bulk solution as shown in Eq. (8):

$$\boldsymbol{N} = C^*_{SO_2} \times a \times \sqrt{D_{SO_2} \times k \times C^{bulk}_{SO_3^{2-}}} \quad (8)$$

where $\boldsymbol{N}$ is the absorption rate of SO_2 (mol m^{-3} s^{-1}); $C^*_{SO_2}$ and D_{SO_2} the solubility and diffusivity of SO_2 in the aqueous phase, respectively; a the interfacial area, k the rate constant for the reaction between SO_2 and SO_3^{2-} ions at the interface and $C^{bulk}_{SO_3^{2-}}$ is the SO_3^{2-} concentration in the bulk of aqueous phase.

Two-film model

In this study, to describe this process in terms of the reaction kinetics, two-film model was used and the reaction rates, mass transfer and diffusion coefficients have been evaluated accordingly. The focus of the gas absorption experiments is based on understanding the mass transfer processes in reactive and non-reactive solvent systems. To model the mass transfer of the gases, it is necessary to generate the absorption kinetics data with or without accompanying chemical reaction. In the two-film model, gaseous molecules in the bulk phase diffuse through a gas–liquid film and then are transferred into the bulk solution; therefore, the total resistance to mass transfer consists of diffusion resistance at the gas–liquid interface and mass transfer resistance in liquid phase.

The overall mass transfer of sulphur atoms from bulk gas phase into chloride solution (mol s^{-1}) may be expressed by Eq. (9):

$$\frac{dm}{dt} = \frac{1}{\left(\frac{1}{k_L} + \frac{1}{k_G}\right)} \times a \times \left(C_{A,i} - C_{A,L}\right) = K \times a \times \left(C_{A,i} - C_{A,L}\right) \quad (9)$$

where $\left(\frac{1}{k_L} + \frac{1}{k_G}\right)$ is the overall mass transfer resistance; K and $\frac{1}{k_G} \approx 0$ since the gas phase is pure with only sulphur atoms. Rate of mass transfer may be rewritten to take into account the constant volume of the solution (mol m^{-3} s^{-1}) and interfacial area (m^2 m^{-3}) exposed to a pure gas phase as shown by Eqs. (10) and (11):

$$d\frac{\left(\frac{m}{V}\right)}{dt} = \frac{dC_{A,L}}{dt} = K_L \times a \times \left(C_{A,i} - C_{A,L}\right) \quad (10)$$

and then reduces to Eq. (8)

$$\frac{dC_L}{dt} = K_L \times a \times (C_i - C_L) \quad (11)$$

where K_L is the mass transfer resistance in the liquid phase. The concentration gradient can be correlated to the pressure drop of the gas during absorption [10].

Methods

Reagents and instruments

All reagents used were pure analytical standard grade solutions purchased from Merck Company (Johannesburg, South Africa). Pure analytical grade SO_2 (99.9 %) gas in pressurized gas cylinders purchased from AFROX (Pty) Ltd, South Africa was used. All standard solutions were prepared in equal concentrations of 100 mg/L using double-distilled water with zero levels of dissolved oxygen. Different concentrations of HCl acid solutions (1.0, 3.0 and 4.0 M) were prepared by diluting HCl acid solution (10 M, 32 % HCl) with known quantities of distilled water. 99.9 % pure analytical grade SO_2 gas in pressurized gas cylinders was used in G–L precipitation tests at moderately high pressure (0.5, 1.0, 1.5 and 2.0 bars). The concentration (99.9 %) and flow rate (177 ml/min) of SO_2 gas were kept constant throughout the tests. The stirring speed (500 rpm) was also kept constant throughout the tests. Barren solution samples which remained after precipitation were analysed for platinum, iron, cobalt and chromium by means of an Inductively Coupled Plasma–Optical Emission Spectrophotometer (ICP–OES) instrument (*Shimadzu model* ICPE–9000). Solid samples (dry precipitates) were analysed using a Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDS). The experiments were carried out using a CSTR, (2L capacity, Büchiglasuster pressure glass vessel autoclave).

Experimental setup

The experiments were carried out in a thermostatted 2-L Büchiglasuster glass reactor as shown in Fig. 1. The reactor is heated by water through a jacketed wall around it. The reactor dimensions are shown in Table 1. The reactor was operated batch-wise with respect to the liquid phase but continuous with respect to the gas phase. The liquid was stirred mildly with a six-bladed Rushton turbine, diameter 50 mm, height 15 mm, located centrally in the liquid at a height above the reactor bottom equal to half the reactor diameter. The gas phase (on top of the liquid phase) was stirred with a three-bladed impeller having a diameter of 50 mm. Both impellers were mounted on a single axis with a diameter of 10 mm. The speed of stirrer was kept constant at 500 rpm throughout the tests. The reactor was equipped with four symmetrically mounted glass baffles with a height of 104 mm and a width of 8 mm. The glass baffles increased the effectiveness of stirring and prevented the formation of a vortex.

Isothermal conditions in the reactor were maintained by circulating hot water from a thermostatted water bath (Tamson T-1000) through the jacket of the reactor. The temperature of the reactor contents was measured by means

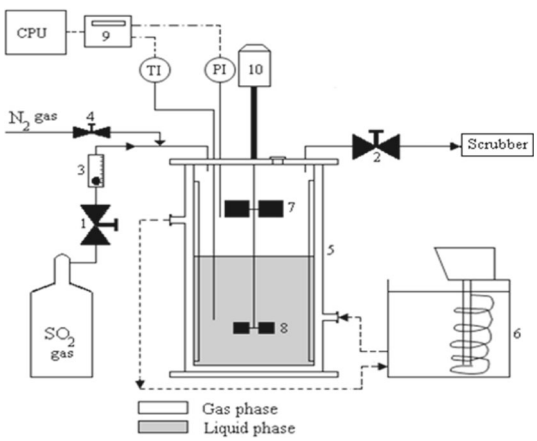

Fig. 1 Stirred cell reactor: SO_2 gas inlet and outlet valves (*1*, *2*); SO_2 gas flowmeter (*3*); N_2 gas inlet valve (*4*); stirred cell reactor (*5*); thermostat water bath (*6*); gas stirrer (*7*); liquid stirrer (*8*); data logger (*9*); magnetic coupling mixer (*10*)

Table 1 Reactor dimensions: continuously stirred tank reactor

Reactor diameter	0.0825 m
Reactor volume	2.0×10^{-3} m^3
Gas–liquid contact area	5.28×10^{-3} m^2 m^{-3}
Liquid impeller type	Six-bladed turbine, 0.05 m diameter
Gas impeller type	Three-bladed turbine, 0.05 m diameter

of a K-type thermocouple. The pressure in the reactor was determined with a Druck PDCR 910 pressure transducer. The pressure and temperature transducers were connected to a Squirrel SQ 1000 series Data Logger and Mercer Premium computer, enabling data collection and programmed reactor operation. A desired mass flow rate of pure SO_2 from the cylinder to the reactor was controlled using a mass flow meter (Brooks 5150 T). The gas leaving the reactor was passed through a caustic scrubber before discharging it to the atmosphere. A pressure regulator was employed to control gas pressure in the reactor (Tescom series 1700 back pressure regulator).

For SO_2 absorption experiments, the gas–liquid reactor was loaded with specific solvent (with or without metal ions in a chloride solution). The concentration of each metal ion was kept constant at 100 mg/L. Acid strength was varied in the range 1–4 M HCl. The reactor content was initially degassed by purging with pure nitrogen gas. The starting solution was allowed to equilibrate with its own saturated vapour at room temperature. The temperature of the metal ion solutions was varied in the range 298 K (25 °C)–313 K (40 °C), after which, at $t = 0$, a feed gas (SO_2) was introduced into the reactor from a high-pressure cylinder possessing a regulator at a constants flowrate of 177 Nml/min. The pressure in the reactor was varied in the range 0.5–2.0 bars (50–200 kPa). Table 2 summarizes the test conditions in the CSTR. After filling the reactor with a SO_2 gas, the stirrer was started and the pressure drop in the reactor was recorded over time. At equilibrium, the pressure drop levelled off and a solution sample was taken from the bulk solution to determine the maximum absorption capacity of SO_2 and amount of precipitate formed. The amount of sulphur sequestered in metal-rich and metal-free chloride solvents (>1 M HCl acid) was recorded. The rate of metal precipitation was not quantified due to difficulties (lack of a sampling gun) associated with solution sampling at high pressure. After 24 h, the composite precipitate from the batch glass vessel was filtered and dried at room temperature. The composite clear filtrate solution remaining was analysed for metal ions using ICP-OES. Dry precipitates were analysed for metal ions and sulphur by means of XRD, SEM and EDS. The flow of the gas was continuous but the liquid was stationary in the vessel. From scale-up point of view, this can be a huge constraint. However, the objective was not to develop parameters for scaling up the process but rather to optimize SO_2 solubility and Pt selectivity at this stage.

Table 2 Experimental conditions: gas–liquid precipitation

Temperature	25–40 °C
Initial pressure	0.5×10^5 Pa
Liquid volume	1.5×10^{-3} m^3
Gas	N_2, purity >99.5 %; SO_2, purity >99.5 % SO_2, purity >99.5 %
Stirrer speed	500 rpm

Results and discussion

Effect of initial metal ion concentration

The feasibility and efficiency of a precipitation process depends not only on the properties of the precipitants, but also on the concentration of the metal ion solution. In this study, the effect of initial concentrations of metal ions (single- and multi-component system) was investigated and the results are illustrated in Figs. 2, 3, and 4.

Figure 2 shows the effect of varying initial Pt and base metal (Fe, Co and Cr) ion concentrations from 50 to 120 mg/L. The data are plotted as SO_2 concentration in the bulk liquid phase versus contact time. The concentration of SO_2 in the bulk liquid phase of chloride solution increased with an increase in initial metal ion concentration. Diffusion is a passive transport process driven by the concentration gradient at the G–L interface. At higher initial metal ion concentration, the driving force for precipitation, which is the difference between the gas phase film concentration and the liquid phase film concentration, is higher. This leads to higher absorption rate in short contact time, for higher initial metal ion concentration. Furthermore, Fig. 2 shows that the absorption capacity sharply increased in the first 10 min (over 80 % gas absorbed) followed by a slower subsequent absorption capacity that gradually approached an equilibrium condition. The average absorption of SO_2

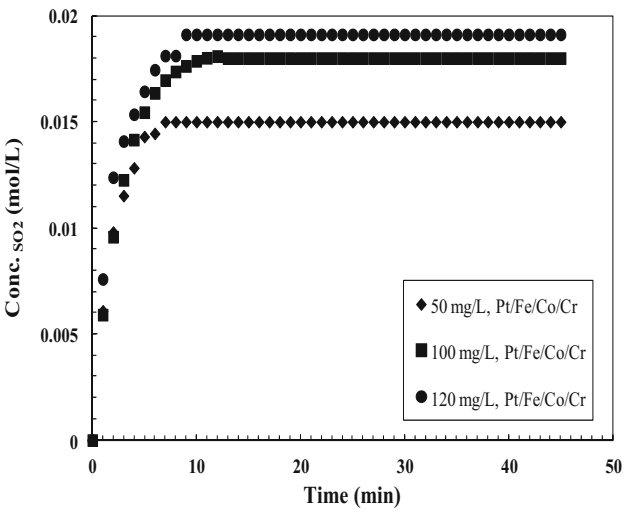

Fig. 2 Effect of initial concentration of multi-metal system (Pt/Fe/Co/Cr) on the absorption of SO_2 in a CSTR. Conditions: $P = 1.125$ bar; $T = 25$ °C; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 4 M; [Me^{n+}] = 100 ppm; contact time = 40 min

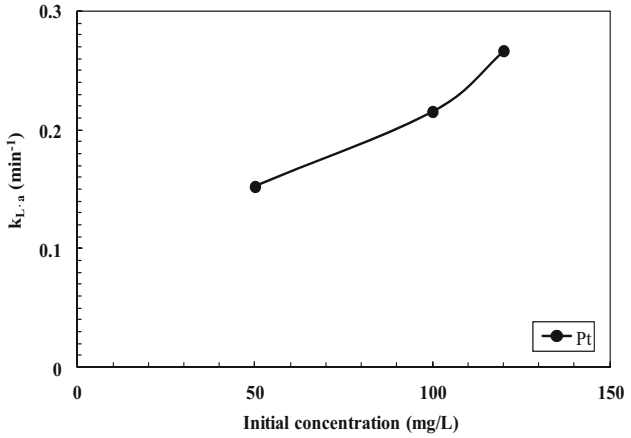

Fig. 3 Mass transfer coefficients vs. initial concentration for Pt ions in chloride system. Conditions: $P = 1.125$ bar; $T = 25$ °C; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 4 M; [Pt^{2+}] = 100 ppm; contact time = 40 min

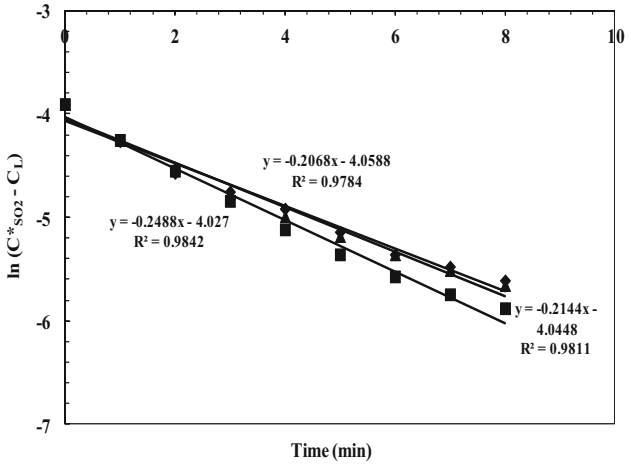

Fig. 4 A plot of $\ln\left(C^{*}_{SO_2} - C_L\right)$ vs. contact time. Determination of mass transfer coefficients for absorption of SO_2 into 4 M HCl chloride solution containing Pt/Fe/Co/Cr ions. Conditions: $P = 1.125$ bar; $T = 25$ °C; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 4 M; [Me^{n+}] = 100 ppm; contact time = 40 min

gas after 10 min was 0.0165 mol/L and recovery of Pt from all chloride solutions averaged above 99 % in less than 10 min. It is evident that the rate of increase of SO_2 concentration in the bulk liquid phase was dependent on the initial metal ion concentration.

The absorption kinetics of SO_2 in chloride solution (4 M HCl) containing Pt/Fe/Co/Cr ions are shown in Figs. 3 and 4, respectively. The rate of mass transfer $K_L \times a$ may be limited by resistance in the gas phase film or liquid phase film. Thus, the $K_L \times a$ values were evaluated using Eq. (11), (Fig. 4); the results are summarized in Table 3. As the initial concentrations were raised, the mass transfer coefficients increased in a non-linear fashion as shown in Fig. 3.

The experimental data in this study indicate that the rate of increase of SO_2 concentration in the bulk liquid phase increased by approximately 18 % when the initial concentration of Pt and base metal ions concentration was doubled from 50 to 100 mg/L, and also increased by approximately 27 % when the initial concentration of Pt and base metal ions was increased from 50 mg/L to 120 mg/L. The high rate of increase of SO_2 concentration in bulk liquid phase was achieved at the initial concentration of 120 mg/L in both cases (Fig. 2). This indicates that metal precipitation with SO_2 was found to follow the two-film theory. The mass transfer coefficients obtained for all metals increased with an increase in metal ion concentrations.

Determination of mass transfer coefficient

Figure 5 illustrates the absorption kinetics of SO_2 in 4 M HCl acid solution at 25 °C and also the gas pressure of SO_2 changing with time. The gas pressure dropped from 1.125 to 0.22 bars within approximately 20 min of contact time (Fig. 5). The corresponding increase in sulphur concentration is shown as a mirror image of the pressure drop. The average absorption of SO_2 after 20 min was 0.018 mol/L. This data imply that physical absorption of SO_2 in concentrated HCl solution is possible at room temperature. The reason why we carried out absorption tests at high HCl acid strength was because the final solution from the elution circuit of Pt recovery comes at high acid concentrations in the range of 3.5–4.0 M, HCl. From the literature, it is known that Pt can only be precipitated out of the solutions at high HCl concentration (>3.5 M) using sodium thiosulphate [11, 12]. The mass transfer coefficient of SO_2 in HCl acid solution was evaluated using Eq. (11) and data points from Fig. 5. Therefore, $\ln\left(C^{*}_{SO_2} - C_{SO_2,i}\right)$ was plotted against contact time according to Eq. (11) and (Fig. 6). The mass transfer coefficient and corresponding concentration values of dissolved sulphur atoms are summarized in Table 4.

From the gas absorption point of view, the mass transfer characteristics of SO_2 from the bulk gas phase into mixed chloride solvents were established. According to the results, it was found out that the presence of metal ions in the solvent accelerated the uptake of sulphur atoms from the gas phase into a liquid phase through a chemical reaction. Dissolved Sulphur (*DS*) atoms react covalently with base metal ions to form insoluble sulphides; however, they interact with platinum chloro-complex anions by exchanging Cl^- and S^{2-} ions. The latter reaction is characterized by a very small activation energy which makes it possible for platinum sulphide to nucleate preferentially. Resistance to diffusion of a species in a pure gas phase was

Table 3 Mass transfer coefficients with metal ions species in chloride system at different initial metal ion concentrations

Metal ions initial conc. (mg/L)	Pt ions		Pt/Fe/Co/Cr ions	
	$K_L \times a\,(\text{min}^{-1})$	$[S^0]_{\text{equiv.}}$ (mol/L)	$K_L \times a\,(\text{min}^{-1})$	$[S^0]_{\text{equiv.}}$ (mol/L)
50	0.1523	0.014	0.2068	0.015
100	0.2155	0.017	0.2144	0.018
120	0.2667	0.018	0.2488	0.019

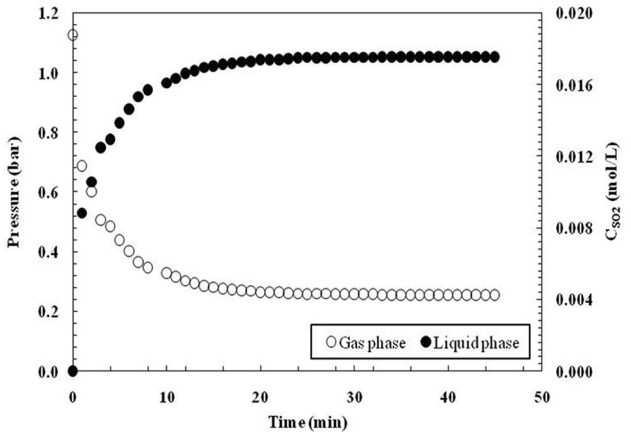

Fig. 5 A plot of pressure drop of SO_2 vs. contact time. Physical absorption of SO_2 into chloride solution at 25 °C. [HCl] = 4 M. In gas phase, the concentration of SO_2 gas was calculated using an ideal gas law. Conditions: $P = 1.125$ bar; $T = 25$ °C; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 4 M; $[Me^{n+}]$ = 100 ppm; contact time = 40 min

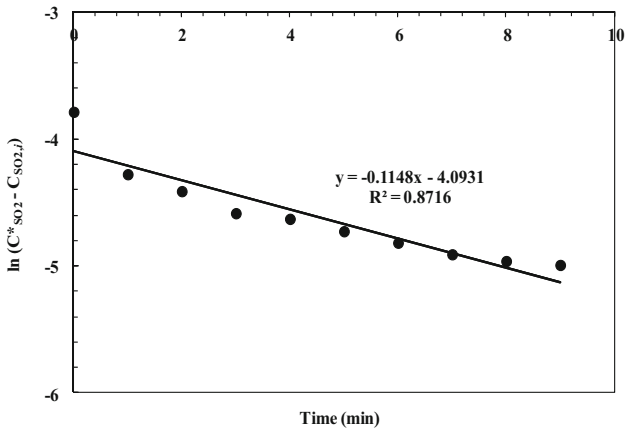

Fig. 6 A plot of $\ln\left(C^*_{SO_2} - C_{SO_2,i}\right)$ vs. contact time. Evaluation of mass transfer coefficient for physical absorption of SO_2 into 4 M (HCl) chloride solution at 25 °C and a gas pressure of 1.125 bars. Conditions: $P = 1.125$ bar; $T = 25$ °C; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 4 M; $[Me^{n+}]$ = 100 ppm; contact time = 40 min

considered to be negligible because the process of pure SO_2 absorption with no suspended particles, allows the gas to dissolve faster and directly in the bulk liquid and dissolved SO_2 can be consumed by reactions in Eq. (5) and Eq. (6) simultaneously. The concentration of SO_3^{2-} in the bulk liquid increases as the absorption process proceeds. Therefore, the mass transfer model of SO_2 was modelled through the absorption kinetics data with or without an accompanying chemical reaction.

Table 4 Mass transfer coefficients with and without metals in solution

System	$K_L \times a\,(\text{min}^{-1})$	$[S^0]_{\text{equiv.}}$ (mol/L)
Physical absorption	0.1148	0.0161
Absorption with *Pt*	0.1575	0.0164
Absorption with *Pt/Fe/Co/Cr*	0.2495	0.0182

Effect of hydrochloric acid concentration on physical absorption of SO_2 gas

Figure 7 shows that the increase in HCl concentration adversely affects the physical absorption of SO_2. In this study, HCl was varied in the range 1–4 M because Pt exists as anionic chloro-complexes in this range. As the concentrations of HCl were increased, the mass transfer coefficient decreased in non-linear form as shown in Fig. 7. The results in Fig. 7 were attributed to the salting-out effect of gaseous molecules in the acidic solution and also probably due to an increase in the interfacial tension at the liquid surface. Platinum ions exist

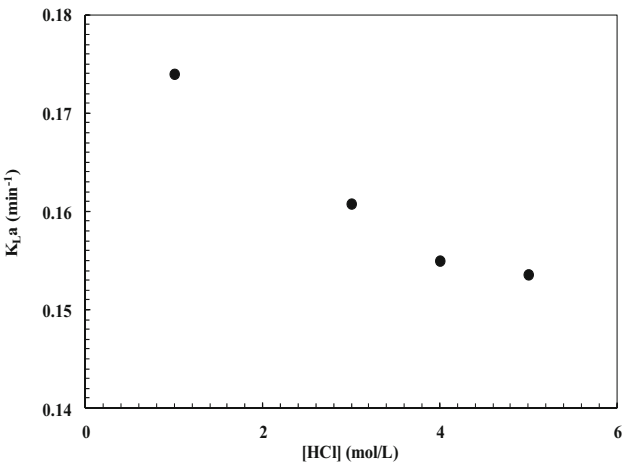

Fig. 7 A plot of mass transfer coefficients in liquid phase vs. [HCl]. Conditions: $P = 1.125$ bar; $T = 25$ °C; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 1–5 M; $[Me^{n+}]$ = 100 - ppm; contact time = 40 min

as stable chloro-complex anions in highly acidic chloride solutions [13]. This implies that the degree of Pt ionization is strongly dependent on the [Cl] concentration.

Thermodynamics parameters

The effect of chloride solution temperature on SO_2 absorption, at constant acid strength (4 M HCl), pressure (1.125 bar), stirring speed (500 rpm) and metal concentration doses (100 mg/L) was studied and the results are shown in Fig. 8. The kinetic experiments were conducted at 298.15, 303.15 and 313.15 K. Figure 8 illustrates that SO_2 solubility was slightly affected by temperature in the range 298.15–313.15 K. It is well known that physical absorption of gases is affected by increase in temperature due to the shift in the vapour liquid equilibrium (VLE). According to the Le Chatelier's principle, when the temperature to a system at equilibrium is increased, the system should move in a direction so that the added heat is absorbed. Thus, an increase in the temperature of a chemical system at equilibrium favours an endothermic reaction. Furthermore, the average kinetic energy of molecules in a gas depends on the temperature. Therefore, when the temperature is increased the gas molecules will move more rapidly and the average kinetic energy of the gas molecules increases. Thermodynamically, gas molecules prefer to exist in the gas phase at high temperatures.

Table 5 illustrates the calculated values of diffusion coefficient, D_L, from Eq. (8) and rate constant, k_R at different temperatures. The diffusion coefficient (D_{SO_2}) values of SO_2 into metal solution in chloride systems increased with temperature as expected and the relationship

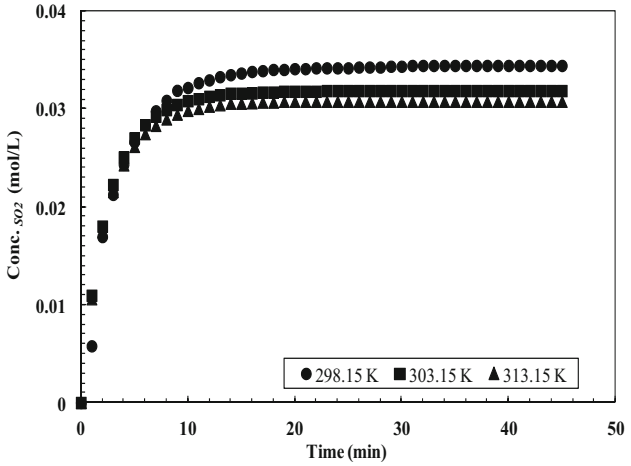

Fig. 8 Dependence of concentration of SO_2 on contact time at different temperatures. The effect of temperature on physical absorption of SO_2 in chloride solution at 298.15, 303.15 and 313.15 K. P = 1.125 bar; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 4 M; $[Me^{n+}]$ = 100 ppm; contact time = 40 min

between diffusion coefficients of SO_2 in metal solution and the temperature is linear as shown in Fig. 9 [14, 15].

The k_R values decrease with temperature due to the fact that k_R is a "phenomenal" constant which corresponds not only to the reaction between SO_2 and metal ions in the solution, but also the total phenomenon where the uptake of SO_2 by metal ions in the solution takes place first [16].

Thermodynamic behaviour of SO_2 absorption was further investigated by considering the dependence of diffusion coefficient on solution temperature (Fig. 9; Arrhenius plot). A change in D_{SO_2} for activation diffusion can be correlated with temperature by use of the Arrhenius-type equation given by:

$$D_{SO_2} = Ae^{-\frac{E_a}{RT}} \tag{12}$$

where A is the pre-exponential factor, R the universal gas constant, T the absolute temperature and E_a the activation energy, representing the minimum energy that the reacting system must attain for the absorption to proceed. The value of activation energy E_a depends on the controlling regime in the absorption process. According to researchers [17], absorption process is said to be film diffusion-controlled when $E_a < 16$ kJ/mol and chemical reaction-controlled when $E_a > 50$ kJ/mol. Linearization of Eq. (12) gives

$$\ln D_{SO_2} = \ln A - \frac{E_a}{RT} \tag{13}$$

The logarithmic diffusional time constant, $\ln D_{SO_2}$, was plotted against the reciprocal of absolute temperature, $1/T$, as shown in Fig. 9. The experimental activation energy was determined from the slope of the plot. An activation energy value of 18.6 kJ/mol was obtained confirming that film diffusion might have been the essential rate-limiting step in the absorption process.

The enthalpy, free energy and entropy changes were also determined. The enthalpy change, ΔH, is given by

$$\Delta H = E_a - RT \tag{14}$$

The enthalpy changes determined according to Eq. (14) were 16.12, 16.08 and 15.99 kJ/mol for chloride solution temperatures of 298.15, 303.15 and 313.15 K, respectively. The positive values of ΔH confirm the endothermic nature of absorption/precipitation process. When absorption is endothermic, the precipitation or recovery of the target ions increases with an increase in solution temperature. On the other hand, the values for the free energy change (ΔG) were calculated at different solution temperature using the following expression:

$$\Delta G = -RT \ln\left(C_{SO_3^{2-}}/C^*_{SO_2}\right) \tag{15}$$

where $C_{SO_3^{2-}}$ is the gas concentration of SO_2 with SO_3^{2-} in the bulk liquid phase of chloride solution at equilibrium

Table 5 Summary of thermodynamic properties of SO_2 absorption in G–L chloride system as a function of temperature

Temperature (K)	D_{SO_2} (10^{-9} m^2/s)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS [J/(mol K)]
298.15	2.36	16.12	−3.14	64.59
303.15	2.89	16.08	−3.16	63.47
313.15	3.43	15.99	−3.24	61.41

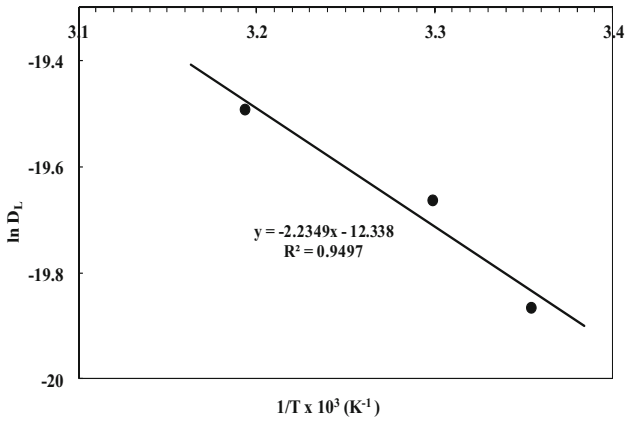

Fig. 9 Dependence of effective diffusion coefficient on temperature: Arrhenius plot. Conditions: $P = 1.125$ bar; T = 298–313 K; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 4 M; $[Me^{n+}]$ = 100 ppm; contact time = 40 min

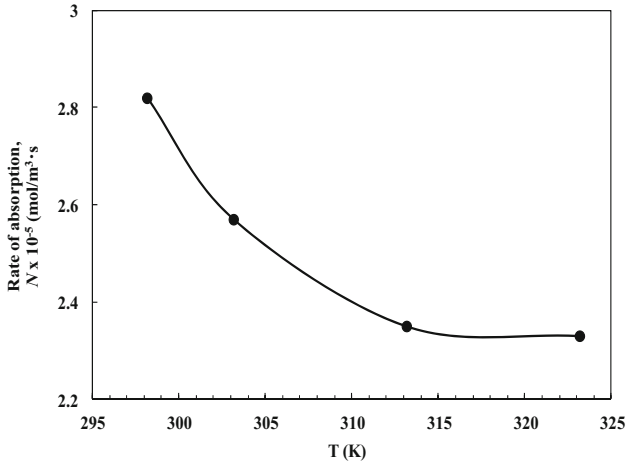

Fig. 10 Effect of temperature on average specific absorption rate. The effect of temperature on physical absorption of SO_2 in chloride media at 298, 303 and 313 K. $P = 1.125$ bar; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 4 M; $[Me^{n+}]$ = 100 ppm; contact time = 40 min

(mol/L), $C^*_{SO_2}$ interfacial concentration of SO_2 (mol/L) at equilibrium. The ΔG values were –3.14, –3.16 and –3.24 kJ/mol for chloride solution temperatures of 298.15, 303.15 and 313.15 K, respectively. The ΔG values indicate the spontaneous nature of absorption of SO_2 into chloride solution. On the other hand, the entropy change (ΔS) was determined according to the expression:

$$\Delta G = \Delta H - T\Delta S \tag{16}$$

ΔS values of 64.59, 63.47 and 61.41 J/(mol·K) for chloride solution temperature of 298.15, 303.15 and 313.15 K, respectively, were obtained. The positive values of the entropy change show the increased mobility or randomness at the gas–liquid interface and an affinity of the absorbent (chloride solution) towards SO_2. The summary of thermodynamic parameters of SO_2 absorption in gas–liquid chloride system as function of temperature is given in Table 5.

Evaluation of absorption rate and diffusivity

The absorption rate (N) and diffusivity (D) values of SO_2 in the chloride system of the continuous stirred tank reactor were evaluated using Eq. (8) considering gas–liquid interfacial area as 0.00528 m^2/m^3 liquid. The absorption rate and diffusivity of SO_2 were in the order of 10^{-5} mol/m^3·s and 10^{-9} m^2/s, respectively.

The absorption rate and diffusivity values of SO_2 were evaluated at different temperatures of the solution in the CSTR (298–313 K). By combining information from Eq. (8), Figs. 8 and 10, absorption rate, diffusivity and rate constant values of SO_2 were evaluated. The results are summarized in Table 6.

Table 6 Effect of temperature on the absorption rate (N), diffusivity (D_{SO_2}) and rate constant (k_R)

T (K)	N (10^{-5} mol/m^3·s)	D_{SO_2} (10^{-9} m^2/s)	k_R (m^3/mol s)
298.15	2.82	2.36	8.81
303.15	2.57	2.89	7.46
313.15	2.35	3.43	6.10

As shown in Fig. 10, the absorption rate is found to decrease considerably with increasing temperature leading to equilibrium state. In the case of gas absorption with accompanying chemical reaction, the absorption rate is influenced by temperature primarily because of two opposing factors: decrease in gas solubility and increase in reaction rate (for irreversible reaction) as the temperature is increased. The experimental data in this study indicate that the rate of absorption decreases by about 17 % for an increase of temperature from 298 to 313 K. For the same change in temperature, the physical solubility and reaction equilibrium constant decreases by 27 % and 10 %, respectively. The fall in physical absorption rate is also

around 27 %. The experimental data further show that the fall in absorption rate in multi-component system (Pt/Fe/Co/Cr) is more sensitive to temperature rise from 303 to 313 K than from 298 to 303 K, compared to the physical absorption rate. This indicates that the reverse reaction rate is more sensitive to temperature than the forward reaction rate. The temperature variation across the liquid film was, however, neglected in the interpretation of data in consideration of the low heat of reaction.

Reactive absorption of SO_2 gas in the presence of metal ion species

In the presence of Pt ions (Fig. 11), the solubility of SO_2 was enhanced slightly due to the chemical reaction with Pt to form Pt–S bond formation. The increase was not significant because the stoichiometric amount of sulphur atoms required to react with the traces of Pt (5.0×10^{-4} mol/L) in solution was small. Initial concentration of Pt was the limiting factor in the reactive solubility of SO_2.

As it can be seen from Tables 3 and 4, the presence of metal ions in the solution has an effect on mass transfer coefficient. The resistance to mass transfer slightly increases as more metal ions are added into a solution. This could be attributed to the fact that interfacial area decreases due to the presence of solid particles in the liquid phase. The formation of solid particles could also influence the effective interfacial area.

Effect of pressure

According to the literature [18], the initial pressures (P_A) are converted to concentrations (C_A) because the rate equations developed in terms of pressures and the calculated values of activation energy are incorrect when these units are used. Therefore, in this study, the initial pressure values of SO_2 were converted into concentration values using the ideal gas law equation given in Eq. (17).

$$P_A V = n_A \boldsymbol{R} T \tag{17}$$

$$P_A = n_A / V \boldsymbol{R} T;\ P_A = C_A \boldsymbol{R} T$$

Therefore,

$$C_A = P_A / \boldsymbol{R} T \tag{18}$$

where $C_A = n_A/V$ is the concentration of component A (mol/L); P_A is partial pressure of component A (bar); V is volume (L); n_A is moles of the component A; $\boldsymbol{R}$ is the ideal gas law constant (L·bar/mol·K) and T is the absolute temperature (K).

Figures 12 and 13 show the plot of SO_2 concentration vs. time and the effect of initial pressure of SO_2 gas on its absorption at ambient conditions, respectively. It is evident from Figs. 12 and 13 that the initial pressure has an effect on gas solubility. It is obvious that SO_2 absorption rate increases as the SO_2 initial pressure increases from 0.5 to 2.0 bars. For instance, the SO_2 absorption rate increases 72.3 % (2.3×10^{-5} to 8.3×10^{-5} mol/m^3·s) at 25 °C as SO_2 initial pressure increases from 0.5 to 2.0 bar. This is due to the fact that SO_2 absorption process under the tested experimental conditions is a gas phase mass transfer control process, as a result, SO_2 initial pressure has a great impact on its absorption rate.

The results in Table 7 show that as initial gas pressure value of SO_2 was increased and the diffusion coefficient values of SO_2 into metal ions solution in chloride systems were increased. Furthermore, it was observed that

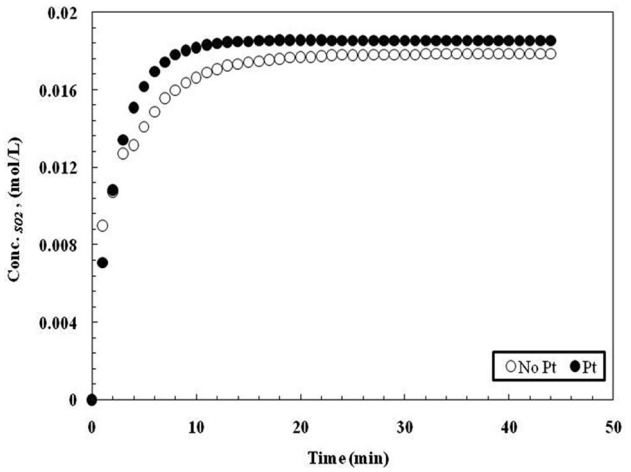

Fig. 11 A plot of SO_2 concentration vs. contact time. Reactive absorption of SO_2 in solution with or without Pt ions. [HCl] = 4 M. P = 1.125 bar; T = 25 °C; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [Me^{n+}] = 100 ppm; contact time = 40 min

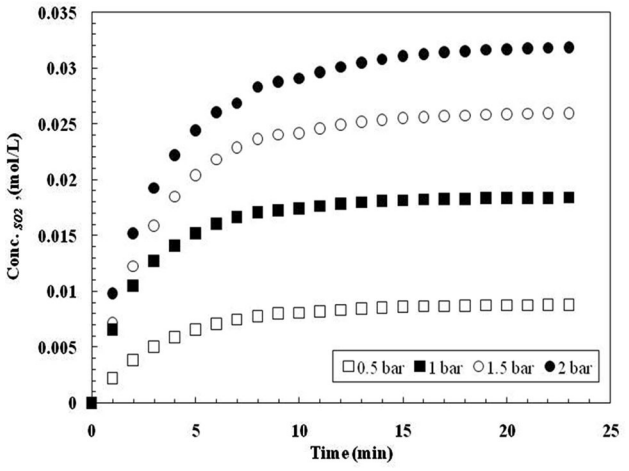

Fig. 12 A plot of SO_2 concentration vs. time. The effect of initial pressure of SO_2 at ambient conditions. Conditions: P = (0.5–2 bar); T = 25 °C; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 4 M; [Me^{n+}] = 100 ppm; contact time = 40 min

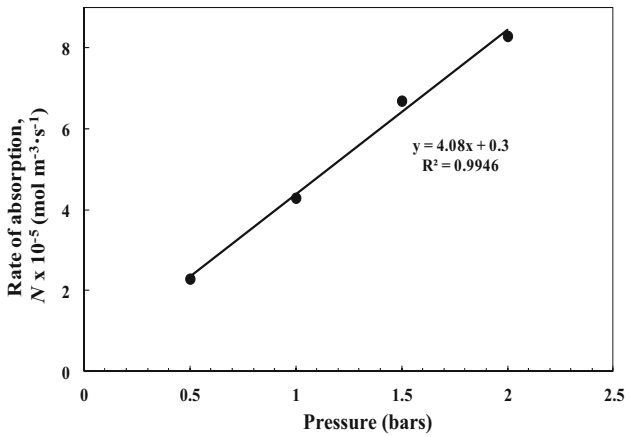

Fig. 13 Effect of SO_2 pressure on its absorption rate at ambient conditions. Conditions: $P = (0.5–2$ bar); $T = 25$ °C; stirring speed = 500 rpm; inlet SO_2 gas conc. = 99.9 vol %; [HCl] = 4 M; $[Me^{n+}] = 100$ ppm; contact time = 40 min

Table 7 Effect of pressure on diffusivity (D_{SO_2}), rate constant, (k_R) in *G–L* chloride system

Pressure (bar)	D_L (10^{-9} m^2/s)	k_R (m^3/mol s)
0.5	1.36	16.60
1.0	1.62	9.82
1.5	1.99	8.52
2.0	2.22	5.20

increasing SO_2 gas concentration (initial gas pressure) increased the rate of metal depletion in solution.

Conclusions

The kinetics study of platinum and base metals precipitation in gas–liquid chloride system using SO_2 was performed in Büchiglasuster glass reactor. Experimental data in G–L chloride system for both physical and reactive absorption conditions indicated the possibility of introducing significant amounts of sulphur atoms in HCl solutions. Sulphur dioxide gas absorption in chloride system was achieved in short contact time while the formation (appearance) of precipitates was achieved after 24 h due to low metal ion concentration. The rate constants were evaluated, which could be used to predict the correct size of industrial contactors. Sulphur atoms exhibited a higher affinity for Pt. The model that best described the diffusion of SO_2 in chloride system was the two-film Model. The mass transfer model of SO_2 was modelled through the absorption kinetics data with or without an accompanying chemical reaction. The absorption rate and diffusivity values in chloride system were evaluated and were found to be in the order of 10^{-5} mol/d^3 s and 10^{-9} m^2 s^{-1}, respectively. The changes in enthalpy (ΔH), entropy (ΔS) and Gibbs' free energy (ΔG) of Pt precipitation were evaluated at optimum temperature of 313.15 K. The positive (ΔS) values and low (ΔG) suggested that some energy is required albeit small for the reactive absorption reaction to proceed. The results from this study confirmed that it is possible to replace liquid precipitants such as $Na_2S_2O_3$ with SO_2 gas as a cost-effective precipitant for Pt.

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